PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:		(11) International Publication Number:	WO 97/09731
H01J	A2	(43) International Publication Date:	13 March 1997 (13.03.97)

(21) International Application Number:

PCT/US96/13330

(22) International Filing Date:

19 August 1996 (19.08.96)

(30) Priority Data:

519,122

24 August 1995 (24.08.95)

US

(71) Applicant: FED CORPORATION [US/US]; Hudson Valley Research Park, 1580 Route 52, Hopewell Junction, NY 12533 (US).

(72) Inventors: JONES, Gary, W.; 181 Academy Street #503, Poughkeepsie, NY 12601 (US). ZIMMERMAN, Steven, M.; 37 Meddaugh Road, Pleasant Valley, NY 12569 (US). SILVERNAIL, Jeffrey, A.; 27 Fairview Avenue, Kingston, NY 12401 (US). JONES, Susan, K., Schwartz; 181 Academy Street #503, Poughkeepsie, NY 12601 (US).

(74) Agent: COYNE, Patrick, J.; Collier, Shannon, Rill and Scott, Suite 400, 3050 K Street N.W., Washington, DC 20007 (US). (81) Designated States: CA, CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

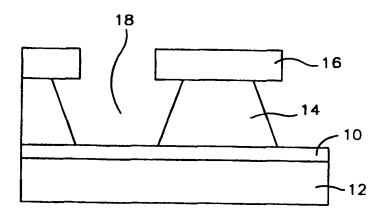
Published

Without international search report and to be republished upon receipt of that report.

(54) Title: FIELD EMITTER DEVICE, AND VEIL PROCESS FOR THE FABRICATION THEREOF

(57) Abstract

A field emitter device formed by a veil process wherein a protective layer (64/66) comprising a release layer (64) is deposited on the gate electrode layer (62) for the device, with the protective layer overlying the circumscribing peripheral edge of the opening of the gate electrode layer, to protect the edge of the gate electrode layer during etching of the field emitter cavity (72) in the dielectric material layer (30) on a substrate, and during the formation of a field emitter element (40) in the cavity by depositing a field emitter material through the opening. The protective layer is readily removed subsequent to completion of the cavity etching and emitter formation steps, to yield the field emitter device. Also disclosed are various planarizing struc-



tures and methods, and current limiter compositions permitting high efficiency emission of electrons from the field emitter elements at low turn-on voltages.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
ΑÜ	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	ΙE	Ireland	NZ	New Zealand
BG	Bulgaria	ΙŢ	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic	SD	Sudan
CF	Central African Republic		of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	Lľ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA.	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

FIELD EMITTER DEVICE, AND VEIL PROCESS FOR THE FABRICATION THEREOF

FIELD OF THE INVENTION

The present invention relates to field emission structures and devices, including field emission-based flat panel displays, as well as to methods of manufacture and use of such structures and devices.

BACKGROUND OF THE INVENTION

In the technology of field emission structures and devices, a microelectronic emission element, or a plurality (array) of such elements, is employed to emit a flux of electrons from one or more field emitters. The field emitter, which often is referred to as a "tip", is specifically shaped to facilitate effective emission of electrons, and may for example be conical-, pyramidal-, or ridge-shaped in surface profile.

Field emitter structures have wide potential and actual utility in microelectronics applications, including electron guns, display devices comprising the field emitter structure in combination with photoluminescent material on which the emitted electrons are selectively impinged, and vacuum integrated circuits comprising assemblies of emitter tips coupled with associated control electrodes.

In typical prior art devices, a field emission tip is characteristically arranged in electrical contact with an emitter conductor and in spaced relationship to an extraction electrode, thereby forming an electron emission gap. With a voltage imposed between the emitter tip and extraction electrode, the field emitter tip discharges a flux of electrons. The tip or tip array may be formed on a suitable substrate such as silicon or other semiconductor material, and associated electrodes may be formed on and/or in the substrate by well-known planar techniques to yield practical microelectronic devices.

Two general field emitter types are known in the art, horizontal and vertical, the direction of electron beam emission relative to the substrate determining the orientational type. Horizontal field emitters utilize horizontally arranged emitters and electrodes to generate electron beam emission parallel to the (horizontally aligned) substrate. Correspondingly, vertical field emitters employ vertically arranged emitters and electrodes to generate electron beam emission perpendicular to the substrate.

Examples of horizontal field emitters are disclosed in Lambe U.S. Pat. No. 4,728,851 and Lee et al U.S. Pat. No. 4,827,177. The Lambe and Lee et al structures are formed as a single horizontal layer on a substrate. An improved horizontal field emitter is disclosed in Jones et al U.S. Pat. No. 5,144,191.

Examples of vertical field emitters are disclosed in Levine U.S. Pat. No. 3,921,022; Smith et al U.S. Pat. No. 3,970,887; Fukase et al. U.S. Pat. No. 3,998,678; Yuito et al U.S. Pat. No. 4,008,412; Hoeberechts U.S. Pat. No. 4,095,133; Shelton U.S. Pat. No. 4,163,949; Gray et al. U.S. Pat. No. 4,307,507; Greene et al U.S. Pat. No. 4,513,308; Gray et al U.S. Pat. No. 4,578,614; Christensen U.S. Pat. No. 4,663,559; Brodie U.S. Pat. No. 4,721,885; Baptist et al U.S. Pat. No. 4,835,438; Borel et al U.S. Pat. No. 4,940,916; Gray et al. U.S. Pat. 4,964,946; Simms et al. U.S. Pat. 4,990,766; and Gray U.S. Pat. No. 5,030,895.

As further examples, Tomii et al U.S. Pat. No. 5,053,673 discloses the fabrication of vertical field emission structures by forming elongate parallel layers of cathode material on a substrate, followed by attachment of a second substrate so that the cathode material layers are sandwiched therebetween in a block matrix. Alternatively, the cathode material layer can be encased in a layer of electrically insulative material sandwiched in such type of block matrix. The block then is sectioned to form elements having exposed cathode material on at least one face thereof. In the embodiment wherein the cathode material is encased in an insulative material, the sliced members may be processed so that the cathode material protrudes above the insulator casing. The exposed cathode material in either embodiment then is shaped into emitter tips (microtip cathodes).

3

Spindt et al U.S. Pat. No. 3,665,241 discloses vertical field emission cathode/field ionizer structures in which "needle-like" elements such as conical or pyramidal tips are formed on a (typically conductive or semiconductive) substrate. Above this tip array, a foraminous electrode member, such as a screen or mesh, is arranged with its openings vertically aligned with associated tip elements. In one embodiment disclosed in the patent, the needle-like elements comprise a cylindrical lower pedestal section and an upper conical extremity, wherein the pedestal section has a higher resistivity than either the foraminous electrode or the upper conical extremity, and an insulator may be arranged between the conical tip electrodes and the foraminous electrode member. The structures of this patent may be formed by metal deposition through a foraminous member (which may be left in place as a counter-electrode, or replaced with another foraminous member) to yield a regular array of metal points.

A metal microtip process conventionally employed in the art to fabricate structures of the type disclosed in the Spindt et al. patent involves the initial fabrication of a basic structure on a substrate of a material such as glass, on which are successively deposited cathode, insulator and gate material layers. The uppermost gate material layer is photomasked, and RIE processed to form an opening in the gate material layer, exposing the underlying insulator layer. The underlying layer of insulator material, e.g., SiO2, is then etched by chemical etch or RIE technique, to yield a cavity below the gate layer opening and extending down to the cathode material layer. This cavity extends radially outwardly under the overlying gate layer, so that the latter forms an overhang over the cavity about its periphery.

Subsequently in this microtip emitter structure formation process, a parting layer is vacuum deposited on the gate layer by evaporation technique, at a shallow angle (e.g., along a direction which is 75 degrees from the central axis of the cavity). The microtip element then is formed in the cavity on the cathode layer with contemporaneous formation of a closure layer overlying the parting layer on the gate structure. Finally, the parting layer is electrochemically etched to remove the closure layer, and yield the final structure in which the gate layer forms a gate electrode structure overlyingly surrounding the conical emitter tip in the cavity.

Jones et al U.S. Pat. No. 5,371,431 discloses a vertical column emitter structure in which the columns include a conductive top portion and a resistive bottom portion, and upwardly vertically extend from a horizontal substrate. By this arrangement, an emitter tip surface is provided at the upper extremity of the column and the tip is separated from the substrate by the elongate column. An insulating layer is formed on the substrate between the columns. An emitter electrode may be formed at the base of the column and an extraction electrode may be formed adjacent the top of the column.

As described in Jones et al U.S. Pat. No. 5,371,431, the vertical column emitter structure may be fabricated by forming the tips on the face of the substrate, followed by forming trenches in the substrate around the tips to form columns having the tips at their uppermost extremities. Alternatively, the vertical column emitter structure of U.S. Pat. No. 5,371,431 is described as being fabricatable by forming trenches in the substrate to define columns, followed by forming tips on top of the columns. In either method, the trenches may be filled with a dielectric and a conductor layer may be formed on the dielectric to provide extraction electrodes.

Further improvements in vertical field emitter structures and fabrication methods are disclosed in Jones U.S. Patent Application Ser. No. 08/627,922 filed April 3, 1996, entitled "Field Emitter Structure and Method of Making the Same," Jones U.S. Patent Application Ser. No. 029,880, filed March 11, 1993, entitled "Emitter Tip Structure and Field Emission Device Comprising Same, and Method of Making Same," and in corresponding International Application Number PCT/US94/02669, published on 15 September 1994 as International Publication WO 94/20975.

SUMMARY OF THE INVENTION

By the present invention, a number of structures are provided which enhance the performance and reliability of field emitter devices, particularly field emitter displays. The invention additionally provides methods for fabricating the structures.

More particularly, the invention provides various improved structures and methods for readily fabricating arrays of field emitter elements in a base structure, in which the field emitter elements have superior uniformity of shape and dimensional character, and resulting enhanced utility for field emitter displays, as compared to field emitter elements formed by prior art fabrication techniques.

BRIEF DESCRIPTION OF THE DRAWINGS

- FIGS. 1-3 depict a process for forming a base structure for subsequent fabrication of emitter tip elements thereon.
- FIGS. 4-6 depict an alternative process to that shown in FIGS. 1-3 for forming a base structure for subsequent fabrication of emitter tip elements thereon.
- FIGS. 7-9 depict the etch formation of emitter tip elements on a base structure of the type formed via the processes of FIGS. 1-3 or FIGS. 4-6.
- FIGS. 10-16 depict the evaporation formation of emitter tip elements on a base structure of the type formed via the processes of FIGS. 1-3 or FIGS. 4-6, with FIGS. 10-12 and 15-16 showing schematically the structures in the processs flow and with FIGS. 13 and 14 showing photomicrographs of the "veiled" precursor structure of the field emission array and of the final field emission array structure.

DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED EMBODIMENTS THEREOF

The present invention relates to a planarization structure for flat-panel video displays using field emitters as electron emitters. The structure (and its variants) permit ease of connection of X and Y grid lines into the active area of a matrix address display.

The insulator stack combination provides for improved isolation between the gate and emitter lines in the vacinity of the emitters by creating an isolation cavity with a long insulator surface up to 2-5 times the thickness of the dielectric, thereby greatly reducing the probability of current leakage across the surface of the insulator near the emitters (due to reduced electric field across the dielectric walls).

Other advantages of the improved field emitter structure of the invention include the following:

- it provides increased physical support of the gate conductor using the upper dielectric layer
- it permits a smoothed surface to be used for the emitter patterning step
- conductive defects are coated in the fabrication of the structure, reducing the probability of electrical shorts resulting from such conductive defects
- the field emitter structure in a preferred embodiment uses spin-on planarized silicon dioxide as part of insulator structure in a unique manner.

Key structural components of an exemplary planarizing structure according to the prresent invention are:

- a spin-on planarizing insulator
- an overlayer of slow etching dielectric
- an etched cavity into the dielectric stack creating a C-shaped cavity with a long dielectric on top
- the accommodation of multiple material layers, thereby building focusing electrodes

In another aspect, the invention contemplates a liftoff structure for fabricating evaporated emitters into the cavities formed in the basic structure.

Key structural components include a multilayer directionally deposited stack comprising:

- 1. A gate conductor (or combination of conductors) e.g., formed of Cr or other useful gate material of construction
- 2. A release layer (e.g., formed of Cu) which can be selectively etched without attack of the gate material
- 3. An optional upper/side veil material with acts to protect the surface sidewalls of the release layer and gate during cavity etching
- 4. An intermediate lithographic liftoff column to create an array of holes when the gate material and release/veil material is deposited.

The foregoing features and aspects are more fully illustrated in the ensuing disclosure, and with reference to the exemplary process embodiments set out hereinafter.

In an illustrative process according to one embodiment of the invention, the field emitter array is formed by the following process steps, as referenced to FIGS. 1-3 hereof.

- 1. Depositing an etch stop layer 10 (FIG. 1), e.g., of SiO, Si₃N₄, or Al₂O₃, on a glass substrate 12 (e.g., with the etch stop layer 10 having a thickness of 0.1 to 2 micron), then depositing a layer 14 of SiO₂ or other suitable insulator material over the etch stop layer to approximately the thickness (e.g., 1 micron) of the subsequently deposited conductor and current limiter layers taken together.
- 2. Patterning the structure formed in step 1 with a photoresist 16 and etching trenches 18 down to the etch stop layer 10 through the silicon dioxide layer 14 (via RIE, plasma, or buffered oxide etch, or a combination of these etching techniques). Overetching is carried out sufficiently to remove SiO2 at the base of the etched cavities so as to accurately set the height of the trench.
- 3. Depositing a bottom conductor material 20, e.g., chromium at a thickness of 1000 Angstroms, and then a layer 24 of a current limiter material such as a layer of SiO + 10% wt. chromium based on the weight of the SiO, at a thickness of for example 6000 Angstroms. The deposition of the current limiter material layer may optionally be preceded and followed by deposition of injector material layers 22 and 26, e.g., of gold or aluminum, at a thickness on the order of 200 Angstroms, depending on the characteristics

desired in the procduct structure (see FIG. 2). Such deposition may be carried out by any suitable method, such as by sputtering or evaporation technique. For example, an Au-(SiO+Cr)-Au film layer structure as shown in FIG. 2 may be employed for a peak current vs voltage device. The top layer may be a combination of etch stop and/or carrier injector layers. The current limiter layer may be masked off the ends of the leads to facilitate subsequent connection of the product display to associated electronics components and circuitry.

- 4. Removing the resist 16 with solvent and liftoff the deposited layers, yielding the structure shown in FIG. 2.
- 5. Spin-on of a planarizing oxide layer 30 (see FIG. 3), of a material such as Dow-Corning FOX (e.g., at a 0.5-2 micron thickness), bake 1 hour at 450 degrees C after slow temperature ramp (3 degrees per minute) to cure. The spin on material may be deposited in multiple coats with intermediate baking steps in the fabrication of this oxide material layer. The resulting structure is shown in FIG. 3.

FIGS. 4-6 depict an alternative process for forming a base structure of the same general type as results from the process depicted in FIGS. 1-3. In this alternative process, as described with reference to FIGS. 4-6, the following steps are carried out:

- 1. Coating resist 16 on the prepared substrate (e.g., a clean glass substrate 12 with an optional pure coating 10 of silicon dioxide or SiO as shown in FIG. 4).
- 2. Depositing the emitter line metal 20, e.g., chromium, and current limiter layer 24 and carrying out liftoff of the resist (in a suitable solvent such as NMP with an IPA rinse) along with the excess metal, yielding the structute shown in FIG. 5. The current limiter may comprise optional injector layers, e.g., of SiO + 20% chromium (wherein the percent of chromium is by weight, based on the weight of the SiO).
- 3. Coating the structure resulting from step 2 with an ~2 micron thickness of a positive resist, baking the resist-coated base, and exposing the resist from the backside using a light

source (e.g., a Hg lamp), developing the exposed resist in a suitable basic developer and baking the resulting structure.

- 4. Depositing insulator 14 onto the front side of the base structure (e.g., SiO2 at a thickness of 1.5 micron) at the same thickness as the combined current limiter 24 and emitter metal 20 thickness, and then carrying out liftoff of the resist 16 with the excess insulator, in a solvent such as NMP with an IPA rinse.
- 5. Depositing a spin-on-oxide (not shown in FIG. 6) to fill in the gaps 25 between the conductor 20/current limiter 24 structures and the deposited insulator 14, and baking/annealing as in the process described in connection with FIGS. 1-3 to achieve a similar resulting base structure.

The base structures resulting from the alternative processes described hereinabove with reference to FIGS. 1-3, and with reference to FIGS. 4-6, respectively, may then be utilized in the formation of field emitter elements thereon, as now described with reference to FIGS. 7-9. The etched emitter tip formation process comprises the steps set out below:

- A.1. Etching back or polishing the spin on oxide 30 to expose the top of the current limiter material 24 or the surface of the injector layer 26 (depending on whether the current limiter material includes an injector layer associated therewith).
- A.2. Optionally depositing an injector layer if not done in a preceding step. unless the emitter material adequately serves this purpose (e.g., silicon with gold doping serves this purpose), and then depositing the emitter material 36, such as silicon or molybdenum (see FIG. 7).
- A.3. Liftoff patterning the emitter material layer 36 with a suitable patterning material, and depositing etch resistant caps 38 (e.g., at a thickness of 50nm to 2,000 nm) thereon, as shown in FIG. 7.

10

A.4. Etching the emitter material 36 first isotropically then anisotropically to form emitters 40, as shown in FIG. 8, and depositing the insulator layers 42, 44, and 46 (e.g., layers 42 and 46 of SiO, and layer 44 of SiO₂) to provide the insulator stack SiO₂/SiO/SiO₂ as shown in FIG. 9.

A.5. Patterning the gate lines for deposition of conductor 48 which may comprise a metal such as Nb or Cr, and carrying out liftoff or etch of the gate lines, followed by etching of the emitter material 36 to sharpen the points 52 and liftoff the caps 38 to complete the emitter array, yielding the product field emitter array article shown in FIG. 9, including a multiplicity of emitter elements 40 each having a cylindrical lower portion 54 and a sharpened tip portion 52.

In accordance with another aspect of the invention, field emitter elements are formed on a base structure by an evaporation process with shielding of portions of the nascent structure during the fabrication by a protective material layer, such process being described below with reference to FIGS. 10-16 and referred to hereinafter as the "veil process" of the invention.

In these Figures, FIGS. 10-16 depict the evaporation formation of emitter tip elements on a base structure of the type formed via the processes of FIGS. 1-3 or FIGS. 4-6, with FIGS. 10-12 and 15-16 showing schematically the structures in the processs flow, and with FIGS. 13 and 14 showing photomicrographs of the "veiled" precursor structure of the field emission array (FIG. 13) and of the final field emission array structure (FIG. 14).

In the practice of the veil process, beginning with a base structure such as formed by the process embodiments illustratively described hereinabove in connection with FIGS.1-3 and FIGS. 4-6 (see FIG. 10), the top surface of the dielectric (spin on oxide) material, layer 30, optionally augmented by the slow etch SiO + SiO2 layer 70, is patterned with a photoresist material, subsequent to which a conductor layer 62 (e.g., of chromium) and a liftoff layer 64 (e.g., of copper) are deposited by sputtering or evaporation. A suitable solvent then is used to liftoff dots of photoresist and metal on top

of such dots, leaving an array of holes in the metal and liftoff layer film. Deposition, pattern, and etch process sequences of varying types may be employed for the purpose of creating a corresponding variety of different structures. Groups of pixels may be patterned in the practice of such fabricational methods, using conventional lithography techniques with steppers, scanners, or holography systems.

The above-mentioned patterns deriving from photoresist patterning of the insulator layer may be exposed in the deposited photoresist using interfered laser beams, since the substrate is free of surface roughness due to the spin-on (oxide deposition) planarization techniques employed. The laser radiation exposure with the interfered laser beams, to carry out the interferometric lithography on the photoresist-coated oxide layer, may by way of example be performed by exposing a line and space interference pattern from a krypton laser (wavelength = ~416 nm) or an argon laser (wavelength = ~351 nm), rotating the substrate 90 degrees, and then reexposing the substrate to laser radiation. A laser interference feedback development system may be advantageously utilized. As a further preferred aspect of such fabricational method, an antireflective layer of a material such as polyimide may be employed, with the antireflective material layer underlying the photoresist. Self-alignment of pixels can be achieved where the emitter leads and gates overlap, even if a coverall dot array pattern is used.

In this interfered laser beam lithographic method, a lithographic mask pattern in addition to the emitter dots may be used to shape arrays of dots into groupings. This mask may also be used to create large dot or line patterns which do not close up during the subsequent emitter material deposition, thereby enhancing the rate and ease of emitter liftoff.

The optional second layer of dielectric 70 may be deposited after curing of the spin-on dielectric (second layer 30 of dielectric shown in FIG. 10), and can be SiO, SiO2, an SiO+SiO2 mixture, or other suitable dielectric material.

By depositing the gate layer 62, release layer 64, and optional upper liftoff layer 64/veil layer 66 at slight angles to the surface of the structure on which the deposition is

carried out, a precursor article as shown in Figure 10 is fabricated. This precursor article provides an ideal liftoff structure for a subsequently evaporatively formed emitter, and enables a fabricational method which is substantially simpler and easier to implement than the prior art methods for forming microtip emitter arrays using shallow angle evaporations.

Sputtering of the gate layer 62, release layer 64, and optional upper liftoff layer 64/veil layer 66 may also be used to create multiple constituent layers as long as build-up of deposited material on the walls of the liftoff columns is suitably controlled with relatively low pressures, as may readily be determined without undue experimentation by those skilled in the art to identify the optimal pressure and other operating conditions for such methodology. In the practice of this methodology, it has been found to be generally advantageous to deposit the release layer 64 and the protective layer (comprising the optional upper liftoff layer 64 and the veil layer 66) at slightly shallower evaporation angles than the angle employed in the deposition of the gate metal layer 62).

The upper veil portion 66 of the protective layer (comprising the optional upper liftoff layer 64 and the veil layer 66) is optional, but helps reduce the sensitivity of the release layer to corrosion during intermediate processing. This veil layer 66 may be formed of any suitable material of construction which is compatible with the liftoff (release) layer 64, and is protectingly effective for the gate conductor layer 62, under the fabricational process conditions to which the veil layer is subjected. Preferred veil layer 66 species include chromium and nickel. FIG. 10 shows the upper portion of the structure as comprising a liftoff cavity 68, which may be formed by any suitable technique, such as RIE, plasma or wet etching techniques, using an etchant medium which is employed after the formation of the liftoff layer 64 but before the formation of the veil layer 66 to etch through the liftoff layer 64 and the conductor layer 62, so that subsequent deposition of the veil layer 66 can be carried out in a manner so that the veil material forms an overcoated portion on the side walls of the liftoff cavity 68 over the liftoff layer as shown in FIG. 10.

The protective layer comprising the optional upper liftoff layer 64 and the veil layer 66 is shown in further detail in FIG. 11, together with the associated gate conductor

13

layer 62, and the slow etch insulator layer 70 (which as mentioned above may comprise Si + SiO2, or other suitable insulator material). As shown in FIG. 11, the protective veil and release material layers cover the edge of the gate conductor layer 62 and the upper protective veil layer 66 ensures that the release layer 64/gate layer 62 is protected at its edge during the cavity etches using RIE, plasma or wet etching. Accordingly, when the emitter material is later deposited in the cavities, excess emitter material will build up on the veil or liftoff layer, and not on the gate edge, thereby promoting a later clean liftoff of the excess emitter material. In this manner, both the release layer 64 and the veil layer 66 are used to create a thin veil structure, which only slightly restricts the cross-sectional area of the emitter cavity and which nonetheless can be lifted off readily in subsequent processing.

Next, a cavity etch step is carried out to form cavities in the dielectric layers 70 and 30, using any suitable etchant medium and technique which is efficacious for such purpose. By way of example, such etching may be carried out using RIE (e.g., with CF4 as the reagent therefor), or via wet processing technique such as BOE, or by a combination of such methods. A wet etch step is preferably used to finish such etching operation, to ensure a clean etch stop on the current limiter material 24/injector layer 26. The resulting cavity-etched structure is shown in FIG. 12, comprising cavity 72.

Subsequent to the formation of the cavities 72 in the dielectric (oxide) layer 30, an emitter material is deposited down into the cavities. The emitter material may be of any suitable material of construction usefully employed in the art for the formation of field emitter elements. By way of example, the emitter material may comprise silicon, or a material such as SiO+50% Cr. The emitter material is deposited by evaporation at low pressure (e.g., <10-5 torr) until the "holes" of the cavity entrances close off, thereby forming a pointed emitter tip under the "close-off" excess emitter material as shown in the photomicrograph of FIG. 13, wherein the precursor article is shown in elevational section, as cut to reveal the interior features of the emitter element and cavity structure. This micrograph is taken at 35.0K magnification, and shows the extremely uniform structural characteristics of the emitter element, and the overlying conformation of the protective layer comprising the liftoff (release) layer and the veil layer.

After formation of the structure shown in the photomicrograph of FIG. 13, the liftoff layer (together with the optional veil layer, if present) is removed, to "reopen" the entrance to the cavity 72. Such protective layer removal may be effected with any suitable reagent which is efficacious for such purpose, with the specific reagent being readily determinable without undue experimentation by those skilled in the art depending on the specific composition of the protective layer. By way of example, nitric acid may be used to release the excess emitter material if a copper liftoff layer is used, and other acid or non-acid removal species may be advantageously employed for other release layer materials.

In removing the protective layer comprising the constituent liftoff layer and (optional) veil layer together with the excess emitter material overcoated thereon, short etches of the gate material layer may be used to separate spurious emitter material depositions on the gate edge. An illustrative etch protocol for such removal is etch removal of ~0.25nm of material thickness where chromium is the gate emitter layer material utilizes potassium permanganate solution 10 wt % in water with ultrasonic agitation at 25°C.

FIG. 14 is a photomicrograph of the resulting field emitter array structure, taken at a magnification of 40.0 K. This micrograph shows the emitter tip element in the cavity of the base structure, with the tip element being overlyingly surrounded by the gate electrode layer, and with the cavity being of smoothly concave contour in the elevationally sectioned view illustrated in the micrograph. The cavity is etched back in the spin-on oxide material layer, so that the overlying dielectric (slow etch material) forms an overhang, and extends the current leakage path between the emitter tip element and the gate electrode, with the slow etch dielectric layer being in turn etched back in relation to the gate electrode layer, so that the gate electrode layer edge at the opening of tip-containing cavity is in appropriate close proximity to the tip element's upper distal end, for highly efficient stimulation of

15

electron emission, at low turn-on voltage, in the operation of the resulting field emission array device.

The details of the field emitter array structure illustrated in the micrograph of FIG. 14 is shown schematically in FIG. 15, and an enlarged elevational view of the cavity portion of such structure is shown in FIG. 16.

As shown in FIGS. 15 and 16, the field emitter array structure comprises the emitter tip element 40 on the injector layer 26 in the cavity 72 formed in the spin on oxide layer 30. The emitter tip element is overlyingly surrounded by the gate electrode 62, beneath which, interposed between the gate electrode and the spin on oxide layer 30 is the slow etch insulator layer 70. The insulator layer 70 is differentially etched back from the periphery of the gate electrode surrounding the upper opening of the cavity 72, so that the gate electrode overhangs the slow etch insulator layer 70. The slow etch insulator layer 70 in turn, as a result of its slower etch character relative to the spin on oxide layer 30, overhangs the spin on oxide at the opening to cavity 72 to provide an extended current leakage path as previously discussed herein.

The emitter element 40 thus is reposed on a pedestal structure comprising bottom conductor 20, injector layer 22, currrent limiter layer 24, and injector layer 26. Such pedestal structure in turn reposes on the dielectric layer 10 formed on the top surface of substrate 10.

The emitter element pedestal support structure on the dielectric layer 10 alternates across the surface of layer 10 with mesa-shaped pedestals 14 of insulator material, with the interstices between these successively alternating pedestals being in-filled with the spin on oxide layer 30.

FIG. 16 shows a close-up enlarged view of the emitter tip element and the surrounding portion of the field emission array structure. As shown in FIG. 16, the emitter tip element 40 is supported on the optional injector layer 26, and in the absence of such layer, the base extremity of the emitter tip element would repose on the top surface

of the current limiter layer 24. The spin on insulator layer 30 is overlaid and overhung by the top insulator layer 70, and the top insulator layer in turn is overlaid and overhung by the gate electrode layer 62. The gate electrode layer may as shown in FIG. 16 have a layer 76 of an insulator material thereon, for the purpose of enhancing the relative electrical isolation of the gate electrode in the overall structure.

In the formation of emitter elements in the practice of the invention, it may be advantageous in some instances to overcoat the emitter tip element with an emitter coating of a suitable low work function material to reduce the work function if a high work function material (e.g., SiO+Cr, or a diamond like film) was employed to form the emitter in the first instance. A sidewall cleanup in the cavity containing the overcoated emitter tip element then may be advantageously carried out, after deposition of the low work function material, to remove the excess low work function material from the sidewalls of the cavity, thereby reducing the gate to emitter electrical leakage which might otherwise be increased in the absence of removal of the excess low work function material.

Suitable low work function coating materials for overcoating the emitter tip elements include: SiO+ 15-80% (by wt., based on the SiO) of chromium; chromium silicides; niobium silicides; or other stable low work function silicides which are oxidizable in air between 350 degrees C and 1000 degrees C (e.g., per a period on the order of 1-12 hours), with 400-500 degrees and an oxidation processing time on the order of 1-4 hours preferred due to the compatibility of such process conditions with the usage of low cost glass as a substrate material.

After formation of the field emission array as described hereinabove is completed, the emitter lines are then lithographically patterned and etched, with an appropriate etchant medium for the emitter line material employed. By way of illustration, potassium permanganate aqueous solution may be employed to etch chromium emitter lines.

Concerning other variations and modifications within the broad scope of the invention that may be utilized in the fabrication of the field emission array product and flat panel display products comprising same, the gate lines for the field emitter array may be

17

deposited from chrome, with a thin gold layer to enhance contact to external leads, by any suitable technique, such as evaporation or sputtering. A thin nickel layer may be deposited over the chromium gate material or in place of the chromium gate material and then immersion coated with gold. Electroless gold or nickel may be used to constrict the gate opening and thicken the gate metal for enhanced conductivity after the leads are patterned.

INDUSTRIAL APPLICABILITY

The field emitter structures and fabrication techniques of the present invention may be employed to manufacture various field emitter-based microelectronics products, including flat panel display devices including field emitter structures in combination with photoluminescent material on which electrons emitted from the field emitter elements are selectively impinged, as well as electron guns, vacuum integrated circuits comprising assemblies of emitter tips coupled with associated control electrodes, and other field emitter-based products.

THE CLAIMS

What is Claimed is:

- 1. A field emitter device comprising a field emitter element reposed on a support structure on a substrate, with a gate electrode overlyingly surrounding the field emitter element, wherein the support structure comprises a current limiter support member formed of a current limiter material comprising silicon monoxide containing from about 5 to about 80% by weight of chrromium, based on the weight of silicon monoxide present in the current limiter material.
 - 2. A field emitter device comprising:
 - a substrate;
- a field emitter support structure comprising a bottom conductor and a current limiter body above said bottom conductor, the field emitter support structure extending upwardly from the substrate, to an upper extremity defining a generally flat surface;
 - a field emitter element on said support structure;
- a layer of planarizing spin on oxide insulator material surrounding the field emitter element and defining a cavity therein containing the field emitter element with cavity side walls in spaced relationship to the field emitter element, and having a flat top surface;
- a layer of a second insulator material, different from the planarizing spin on oxide insulator material, on the flat top surface of the planarizing spin on oxide insulator material, said second insulating material layer extending overhangingly over the cavity to provide an extended current leakage path; and

a gate electrode layer on the layer of second insulator material, and extending overhangingly over the second insulator material layer and over the cavity to a gate electrode layer edge circumscribing an upper portion of the field emitter element.

- 3. A field emitter device according to claim 2, wherein the second insulator material has an enhanced etch resistance characteristic relative to the planarizing spin on oxide insulator material.
- 4. A field emitter device according to claim 2, wherein the field emitter support structure is reposed on said substrate with an intermediate layer of a dielectric material between the substrate and the field emitter support structure.
- 5. A field emitter device according to claim 2, wherein the field emitter support structure is laterally adjacent block members of insulator material, with space between the field emitter support structure and each said laterally adjacent block member of insulator material, with the planarizing spin on oxide insulator material layer overlying the field emitter and laterally adjacent block members of insulator material, and filling the space between them.
- 6. A field emitter device according to claim 2, wherein the field emitter support structure comprises a first layer of an electron injection material between the bottom conductor and the current limiter body, and a second layer of an electron injection material between the current limiter body and the field emitter element.
- 7. A field emitter device according to claim 6, wherein the first and second electron injection layers are formed of a metal selected from the group consisting of aluminum and gold.
 - 8. A field emitter device precursor article, comprising:
 - a substrate;

an insulator material on the substrate defining a cavity for vapor phase deposition formation of a field emitter element therein, said cavity having an upper opening for discharge of electrons from said field emitter element through said upper opening;

a gate conductor layer on the insulator material for circumscribing the field emitter element and defining a circumscribing peripheral edge in spaced relationship to said field emitter element, said circumscribing peripheral edge in turn defining an opening in the gate electrode layer which is aligned with the upper opening of the cavity; and

a protective layer over the gate conductor layer, said protective layer (i) comprising a liftoff layer on the gate conductor layer, and (ii) extending over said circumscribing peripheral edge of said gate conductor layer to restrict deposition field emitter element forming material on said gate conductor layer circumscribing peripheral edge during said vapor phase deposition formation of said field emitter element.

- 9. A field emitter precursor article according to claim 8, wherein the protective layer comprises a veil layer over the liftoff layer, with said veil layer overlying the circumscribing peripheral edge of said gate conductor layer.
- 10. A field emitter precursor article according to claim 8, wherein the liftoff layer comprises copper, and the veil layer comprises a metal selected from the group consisting of chromium and nickel.
 - 11. A field emitter device precursor article, comprising:

a substrate;

an insulator material on the substrate defining a cavity containing a field emitter element therein, said cavity having an upper opening for discharge of electrons from said field emitter element through said upper opening; WO 97/09731

a gate conductor layer on the insulator material circumscribing the field emitter element and defining a circumscribing peripheral edge in spaced relationship to said field emitter element, said circumscribing peripheral edge in turn defining an opening in the gate electrode layer which is aligned with the upper opening of the cavity;

a protective layer over the gate conductor layer, said protective layer (i) comprising a liftoff layer on the gate conductor layer, and (ii) extending over said circumscribing peripheral edge of said gate conductor layer to restrict deposition field emitter element forming material on said gate conductor layer circumscribing peripheral edge during said vapor phase deposition formation of said field emitter element; and

an overlayer of excess deposited field emitter element forming material on said protective layer which at least partially occludes said upper opening of the cavity.

12. A field emitter structure for use in a field emitter device to emit electrons therein, said field emitter structure comprising a main body portion of a first material having a first relatively higher work function characteristic, and overcoated with a second material having a second relatively lower work function characteristic, wherein the second material is selected from the group consisting of:

SiO + 15-80% (by wt., based on the SiO) of chromium; and

metal silicides which are oxidizable in air at a temperature of from about 350 degrees Centigrade and 1000 degrees Centigrade during a heating period of from about 1 to about 12 hours.

13. A field emitter structure according to claim 12, wherein said second material is selected from the group consisting of:

SiO + 15-80% (by wt., based on the SiO) of chromium; chromium silicides; and niobium silicides.

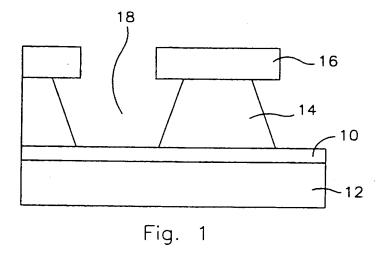
22

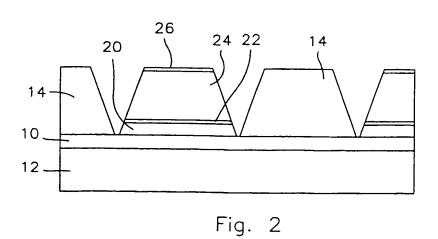
- 14. A field emitter structure according to claim 12, wherein said second material is oxidizable in air at a temperature of from about 400 degrees Centigrade and 500 degrees Centigrade during a heating period of from about 1 to about 4 hours.
- 15. In a method of making a field emitter device including the steps of (i) etching a cavity in a dielectric material layer on a substrate wherein the dielectric material layer is overlaid by a gate electrode layer having an opening therein for communicating with said cavity, with said opening bounded by a circumscribing peripheral edge of said gate electrode layer defining said opening, and (ii) forming a field emitter element in said cavity by depositing a field emitter material through said opening,

the improvement comprising: depositing on said gate electrode layer a protective layer comprising a release layer, with the protective layer overlying the circumscribing peripheral edge of said gate electrode layer defining said opening therein, to protect said edge of the gate electrode layer during said steps (i) and (ii), and removing said protective layer subsequent to completion of said steps (i) and (ii), to yield said field emitter device.

16. A method according to claim 15, wherein the protective layer comprises an underlying release layer formed of copper and an overlying veil layer formed of chromium or nickel.

1/8





SUBSTITUTE SHEET (RULE 26)



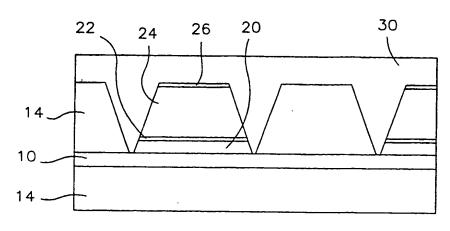


Fig. 3

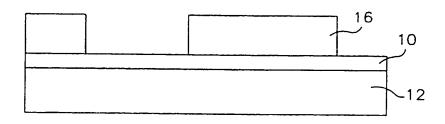


Fig. 4

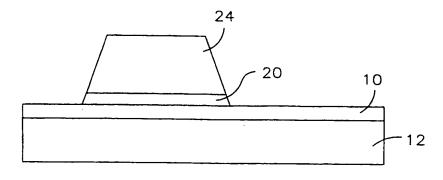
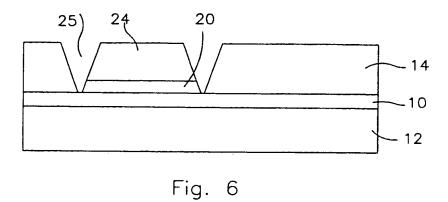
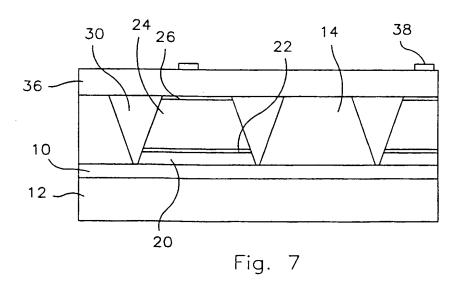


Fig. 5

SUBSTITUTE SHEET (RULE 26)

3/8





SUBSTITUTE SHEET (RULE 26)

4/8

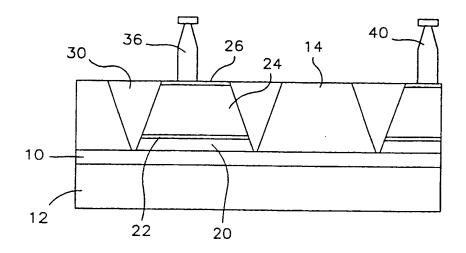


Fig. 8

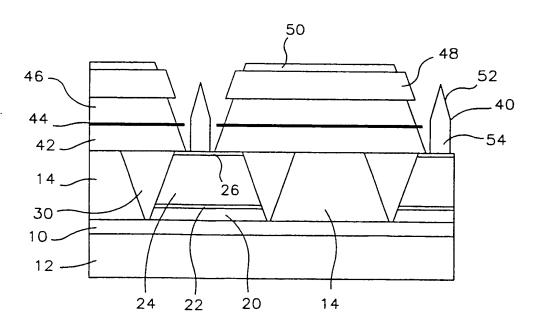
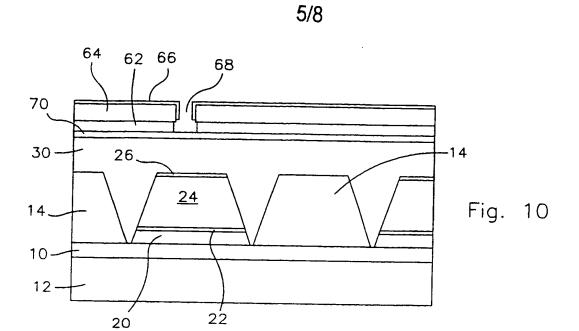
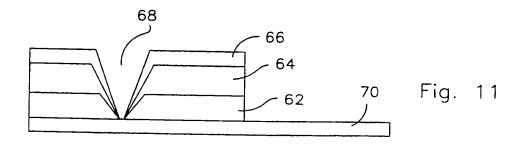
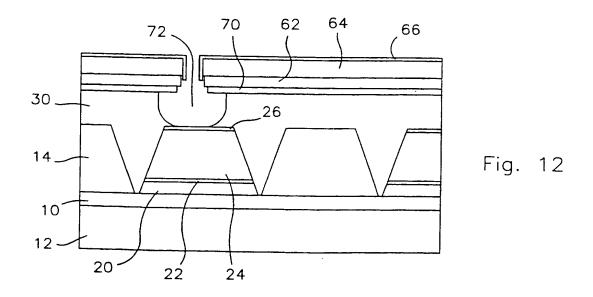


Fig. 9

WO 97/09731







SUBSTITUTE SHEET (RULE 26)

6/8

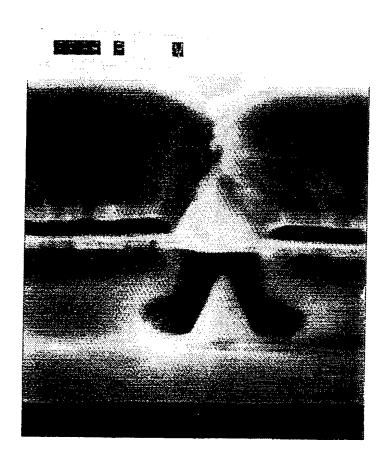


FIG. 13

7/8

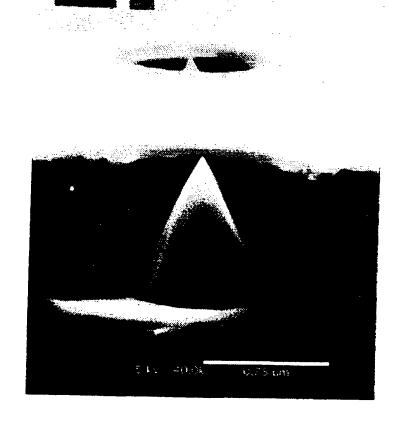


FIG. 14

SUBSTITUTE SHEET (RULE 26)

8/8

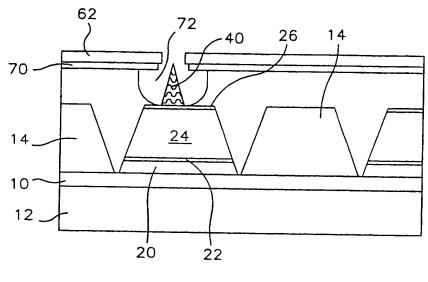
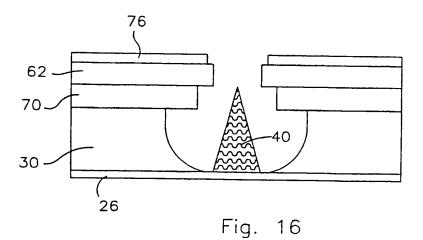


Fig. 15



SUBSTITUTE SHEET (RULE 26)



WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:

H01J 1/32, 9/18

A3

(11) International Publication Number:

WO 97/09731

(43) International Publication Date:

13 March 1997 (13.03.97)

(21) International Application Number:

PCT/US96/13330

(22) International Filing Date:

19 August 1996 (19.08.96)

(30) Priority Data:

519,122

24 August 1995 (24.08.95)

US

(71) Applicant: FED CORPORATION [US/US]; Hudson Valley Research Park, 1580 Route 52, Hopewell Junction, NY 12533 (US).

(72) Inventors: JONES, Gary, W.; 181 Academy Street #503, Poughkeepsie, NY 12601 (US). ZIMMERMAN, Steven, M.; 37 Meddaugh Road, Pleasant Valley, NY 12569 (US). SILVERNAIL, Jeffrey, A.; 27 Fairview Avenue, Kingston, NY 12401 (US). JONES, Susan, K., Schwartz; 181 Academy Street #503, Poughkeepsie, NY 12601 (US).

(74) Agent: COYNE, Patrick, J.; Collier, Shannon, Rill and Scott, Suite 400, 3050 K Street N.W., Washington, DC 20007 (US).

(81) Designated States: CA, CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

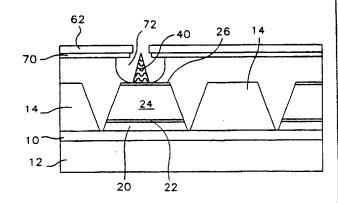
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(88) Date of publication of the international search report:
03 April 1997 (03.04.97)

(54) Title: FIELD EMITTER DEVICE, AND VEIL PROCESS FOR THE FABRICATION THEREOF

(57) Abstract

A field emitter device (Figure 15) formed by a veil process wherein a protective layer including a release layer is deposited on a gate electrode layer (62) for the device, the protective layer overlaying the circumscribing peripheral edge of the opening of the gate electrode layer (62) to protect the edge of the gate electrode layer (62) during etching of a field emitter cavity (72) in a dielectric material layer (30) on a substrate (12) and during the formation of a field emitter element (40) in the cavity by depositing a field emitter material through the opening (72). The protective layer is readily removed subsequent to completion of the cavity etching formation steps, to yield the field emitter device. The field emitter device further includes a current limiter composition (14) for permitting high frequency emission of electrons from the field emitter element (40) at a low turn-on voltage.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE.	
BB	Barbados	GR	Greece .	NL NL	Niger Netherlands
BE	Belgium	HU	Hungary	NO.	
BF	Burkina Faso	IE	Ireland		Norway
BG	Bulgaria	IT	Italy	NZ	New Zealand
BJ	Benin	JР	Japan	PL	Poland
BR	Brazil	KE	Kenya	PT	Portugal
BY	Belarus	KG	Kyrgystan	RO	Romania
CA	Салада	KP	- 	RU	Russian Federation
CF	Central African Republic	KI	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR		SE	Sweden
CH	Switzerland		Republic of Korea	SG	Singapore
CI	Côte d'Ivoire	KZ	Kazakhstan	SI	Slovenia
CM		LI	Liechtenstein	SK	Slovakia
CN	Cameroon	LK	Sri Lanka	SN	Senegal
	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Мопасо	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

INTERNATIONAL SEARCH REPORT

International application No. PCT/US96/13330

1	SSIFICATION OF SUBJECT MATTER:		
US CL	:313/310	and and along Continuous LINC	
	to International Patent Classification (IPC) or to both LDS SEARCHED	national classification and IPC	
	locumentation searched (classification system followe	d by classification symbols)	
U.S. :	313/310, 306, 309, 311, 336, 351, 495, 496; 156/62	25.1, 647.1, 654.1	
Documental	tion searched other than minimum documentation to th	e extent that such documents are included	in the fields searched
Electronic o	data base consulted during the international search (ne	ame of data base and, where practicable	, search terms used)
C. DOC	CUMENTS CONSIDERED TO BE RELEVANT		
Categorya	Citation of document, with indication, where a	opropriate, of the relevant passages	Relevant to claim No.
Х, Р	US, A, 5,529,524 (JONES) 25 June 1996, Figures 29, 40, 43c, 61, 70, 92, 123-125, 132-133, 151-152; col. 10, line 18-col. 12, line 67; col. 16, line 58-col. 17, line 26; col. 26, line 37-col. 28, line 4; col. 29, line 35-col. 30, line 32; col. 33, line 11-col.34, line 10		1-16
A	US, A, 5,075,591 (HOLMBERG) 2 2; col. 3, lines 37-58	2-4, 12	
A	US, A, 5,404,070 (TSAI ET AL) 04 APRIL 1995, Figures 3a, 4-6, 12, 13; col. 3, line 20-col. 4, line 11		15-16
A	US, A, 3,970,887 (SMITH ET AL 1g, 7; col. 4, line 36-col. 6, line 7		15-16
Furth	I her documents are listed in the continuation of Box C	See patent family annex.	<u></u>
·A· do	pecial categories of cited documents: comment defining the general state of the art which is not considered be of particular relevance	"T" later document published after the inte date and not in conflict with the applic principle or theory underlying the inv	otion but cited to understand the
	rtier document published on or after the international filing date	"X" document of particular relevance; the considered novel or cannot be considered.	
cit	ecument which may throw doubts on priority claim(a) or which is led to establish the publication date of another citation or other ecial reason (as specified)	"Y" document of particular relevance; the considered to involve an inventive	
	ecument referring to an oral disclosure, use, exhibition or other eans	combined with one or more other suc being obvious to a person skilled in the	h documents, such combination
	ecument published prior to the international filing date but later than e priority date claimed	*&* document member of the same patent	formily
Date of the actual completion of the international search Date of mailing of the international search report		arch report	
10 ОСТО	DBER 1996	21 FEB 1997	/
Commission Box PCT	mailing address of the ISA/US oner of Potents and Trademarks	Authorized officer A MARCA ASHOK PATEL	orturn
Facsimile N	n, D.C. 20231 No. (703) 305-3230	Telephone No. (703) 305-4900	

Form PCT/ISA/210 (second sheet)(July 1992)#

INTERNATIONAL SEARCH REPORT

International application No. PCT/US96/13330

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows: Telephone Practice Group I. Claims 1-7 and 12-16, drawn to a field emitter structure, a field emitter device and a method of making the field emitter device, Group II. Claims 8-11, drawn to a field emitter device precursor article.
1. X As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
The additional search fees were accompanied by the applicant's protest. X No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1))(July 1992)*